Acceptor Luminescence in High-Purity *n*-Type GaAs†

J. A. Rossi, C. M. Wolfe, and J. O. Dimmock
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173
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Photoluminescence of epitaxial GaAs in a magnetic field has established the origin of several recombination transitions 20 to 40 meV off the band edge. The data indicate that two acceptor levels are present in high purity material and that two free-electron—neutral-acceptor and two donor-acceptor pair bands are observed in photoluminescence at low temperatures.

At present there exists considerable disagreement among the various workers as to the recombination mechanisms responsible for the low-temperature luminescence at energies 20 to 40 meV below the band edge of high-purity GaAs.[1-8] We have studied the luminescence of various epitaxial GaAs samples grown in this laboratory as a function of impurity concentration, incident light intensity, temperature, and electric and magnetic fields. Among these several techniques, the magnetic-field data provide us with the most information about the nature of the recombination transitions. From our results we conclude that there are two acceptors participating in the observed photoluminescence in all of the samples reported here and probably elsewhere.[2-6,8]

For normal photoluminescence measurements the samples were mounted in a strain-free manner in a variable-temperature Dewar. The samples were excited at normal incidence by a cw He-Ne laser (~15 mW) and the sample luminescence was gathered from the excited surface. For the magnetic-field measurements, the samples were mounted in an immersion (4.2°K) Dewar with the applied magnetic field perpendicular to the excited sample face. The sample light was dispersed by a Jarrell-Ash 1-m spectrometer and detected with an S-1 photomultiplier cooled by dry nitrogen gas. Standard dc detection was used throughout these experiments.

All samples used were grown in an effort to obtain high-purity GaAs. The donors and acceptors present are therefore residual and not intentionally introduced dopants. No correlation of the acceptor photoluminescence spectra with the presence or absence of specific chemical impurities will be attempted here. We have examined two dozen samples with impurity concentrations in the range 7×10^{13} cm$^{-3} \leq N_D+N_A \leq 5\times10^{15}$ cm^{-3}. The samples discussed here were selected because they accurately represent the different photoluminescence spectra observed by previous workers[1-8] and by us in samples with low total electrically active impurity content. All of the samples are n type; the values of N_D and N_A for each sample (cf. Fig. 1) are calculated from Wolfe, Stillman, and Dimmock.[9]

We show as the bottom two traces in Fig. 1 typical photoluminescence spectra obtained from two different samples at 4.2°K with no applied magnetic field. For simplicity we have omitted the near-edge emission (at higher energies) and phonon replicas (at lower energies) as they are not germane to the discussion presented here. Note that each sample is dominated by a pair of luminescence peaks (the position in energy of each peak is given in Fig. 1). The samples appear to have the 1.4861 and 1.4933 eV transitions in common. Spectra similar to the left-hand curve (sample A) have been reported in Refs. 1, 3, and 7, and spectra similar to the right-hand trace (sample B) have been reported in Refs. 2, 4, 5, and 6.

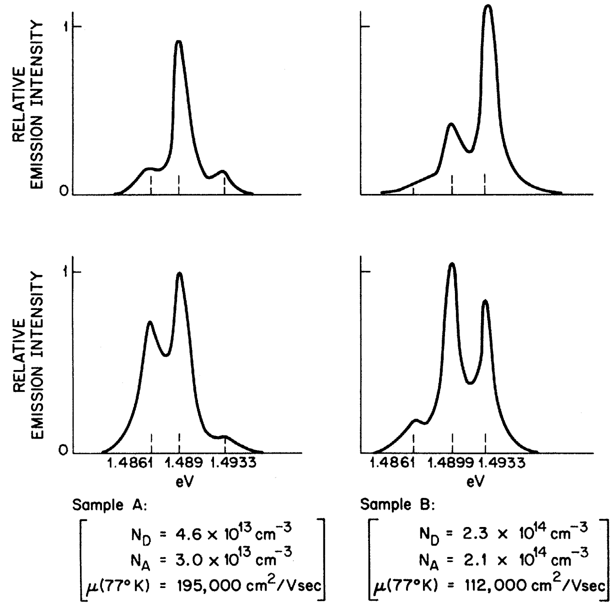

FIG. 1. Pertinent photoluminescence spectra from two GaAs epitaxial layers. The bottom two traces were taken with each sample at 4.2°K, the upper two at 10°K.

The upper traces in Fig. 1 show the effect of increasing temperature on the sample luminescence. Each sample has one peak which rapidly grows in intensity (A, 1.4890 eV and B, 1.4933 eV) and one which rapidly falls (A, 1.4861 eV and B, 1.4899 eV). Temperature effects similar to these have been reported in every GaAs photoluminescence paper in which the peaks were observable and the temperature was varied.[2-6,8] With increased N_D and N_A, the behavior may be observed at higher temperatures,[3] but it is always observed. Although we do not consider the temperature data conclusive, they suggest that similar recombination mechanisms are operative in both crystals but as slightly different energies.

Figure 2 shows the effects of a magnetic field on the various recombination peaks. In Fig. 2(a) the shift in the peak position of the 1.4933-eV (solid circles) and 1.4890-eV (open circles) transitions are plotted against magnetic field. We have data similar to this for many different samples. Note that both transitions move linearly in H to higher energy, and both do so at the same rate. In Fig. 2(b) the shifts in the peak positions of the 1.4899-eV (solid triangles) and 1.4861-eV (open triangles) transitions are plotted against H. These shifts are roughly quadratic in H, and again the rates of shift for each are the same. We resolve no splitting of these lines in fields $\lesssim 40$ kG which is consistent with small g factors for electrons and holes.[10] The solid line in Fig. 2(a) will be discussed below.

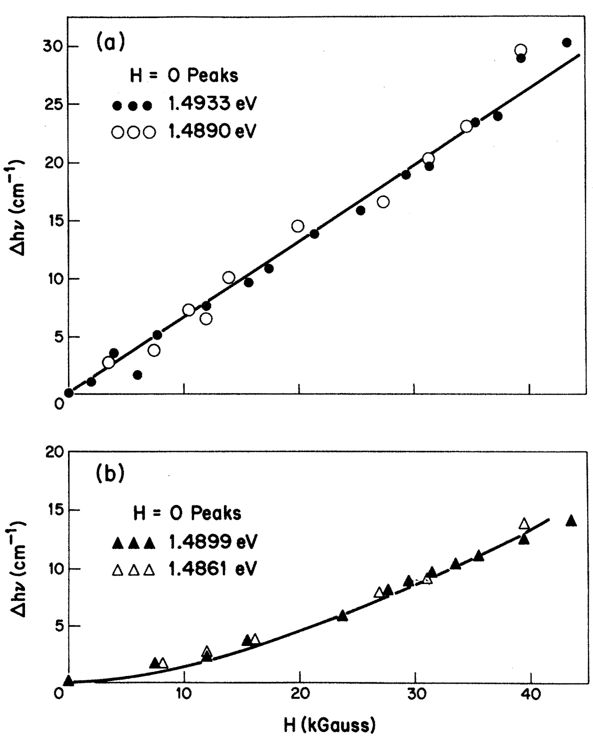

FIG. 2. (a) Behavior of the 1.4933-and 1.4890-eV peaks in a magnetic field. Both peaks move linearly in H. (b) Shifts of the 1.4861-and 1.4899-eV transitions in H. As in (a), both transitions move at the same rate.

Considering for the moment only one free-electron–neutral-acceptor transition (e, A^0), in zero magnetic field we have

$$h\nu(e, A^0) \simeq E_c - E_A, \tag{1}$$

where E_c is the bottom of the conduction band and E_A is the acceptor energy level. As is well known, in a magnetic field the conduction band is broken into several magnetic sub-bands. Considering only the bottom-most level ($n=0$), in a magnetic field the recombination peak will now be at

$$h\nu(e, A^0; H) = E_c - E_A + \frac{e\hbar H}{2m^*c} - \Delta E_A(H). \tag{2}$$

The shift in energy is given by the difference between expressions (1) and (2). The straight line in Fig. 2(a) is drawn with slope $e\hbar/2m^*c$, with $m^* = 0.072m_0$. The slight discrepancy from the measured value[12] of electron mass at the bottom of the band of $0.0665m_0$ is probably due to a band-filling effect which is larger at low magnetic fields and decreases at large fields due to the increase in the density of states at the bottom of the band. This results in a reduction of the slope of $\Delta h\nu$ vs H and an increase in calculated value of m^*. Except for this effect, the excellent fit to the data by a straight-line dependence confirms the identification of both the 1.4933 and 1.4890 eV transitions as free-electron–neutral acceptor. Considering the depth of the binding energies for the two acceptors (~27 and 31 meV), we except $\Delta E_A(H)$ to be small, ~0.2 cm^{-1} at 40 kG. At higher fields we would expect E_A to shift, leading to an even faster increase in $h\nu(e, A^0; H)$.

The temperature data (cf. Fig. 1, and Refs. 2, 3, 5, and 6) further support this assignment. As shown in Fig. 1, both the 1.4933- and 1.4890-eV transitions gain in intensity as the temperature is increased. This is quite consistent with an increase in the concentration of free electrons as seen in the Hall measurements for these same samples (thermal ionization of shallow donors).[13] Application of a small dc bias (~1 V), sufficient to impact-ionize the shallow donors, also greatly enhances the (e, A^0) transitions.

The linewidth of these transitions diminishes as the intensity of the exciting source is reduced.[1]

Since at these concentrations we can neglect the spread in E_A, the controlling factors on linewidth are n_0, the thermal equilibrium concentration of free electrons, and δn, the added steady-state concentration due to the light. Regardless of n_0, i.e., ignoring for the moment compensation, as the incident light intensity is reduced the transition linewidth also decreases. An excellent picture of this effect is shown in Ref. 1, Fig. 8. As compensation is introduced, the value of n_0 will be diminished and a given value of δn will now effect a different and in fact even smaller linewidth than before. We confirm the observation (Refs. 1 and 7) that at low excitation intensities the linewidths may be $<kT$. This trend is consistent with the (e, A^0) model.

At variance with the earlier assignments of exciton–ionized acceptor[1,2,7] and donor-excited-state–acceptor recombination models[3] we conclude that the correlation of the magnetic field, temperature, intensity, electric field, and linewidth data leave no doubt as to the assignments of the 1.4933- and 1.4890-eV transitions as free-electron–neutral-acceptor recombination.

We now discuss the recombination peaks at 1.4861 and 1.4899 eV. First, we note that the transitions always occur in these pairs (1.4861, 1.4890) and (1.4899, 1.4933). In every published paper dealing with GaAs of low total electrically active impurity concentration (Refs. 1-8) pairs of lines in this spectral range have been observed. The observer may have to operate above 4.2°K depending on impurity concentration,[3-5] but eventually pairs of lines (or a shoulder developing on one line if the doping is high enough) are always seen. There are samples in which all four peaks are separately distinguishable, there are other samples in which either one pair or the other is completely dominant, and there are samples exhibiting only three peaks due to the overlap of the 1.4890 and 1.4899 eV transitions. Earlier proposed assignments of the 1.4861- and 1.4899-eV lines associated with the (e,A^0) 1.4890- and 1.4933-eV lines, respectively, include the phonon sideband model,[1-7] exciton ionized-acceptor (X, A^-) recombination,[2-6] and donor-acceptor pair recombination.[2-6,8] The magnetic-field data rule out the phonon sideband model, since the lines do not shift linearly in a magnetic field.

The photoluminescence of these two bands under varying light intensity clearly displays the characteristics of donor-acceptor pair recombination. In Fig. 3 we plot the separation in energy between the peak positions of each associated pair (i.e., $h\nu_{1.4933}-h\nu_{1.4899}$ and $h\nu_{1.4890}-h\nu_{1.4861}$) as a function of incident light intensity. The higher energy pair is plotted as solid triangles and the lower energy pair as open triangles. For reference, all the data in Figs. 1 and 2 were taken at $I/I_0=1$. As the incident intensity is decreased, 1.4933- and 1.4890-eV transitions remain essentially fixed in energy so that the data in Fig. 3 reflect only the shift of associated lower energy bands to longer wavelength. The data show that as I/I_0 is decreased the energy difference between the peaks increases, reaching ~4.3 meV at $I/I_0 \simeq 10^{-3}$. Lower intensity measurement have not been possible. The energy of donor-acceptor pair recombination is given approximately by

$$h\nu(D^0, A^0) = E_D - E_A + e^2/\kappa R_{DA}, \tag{3}$$

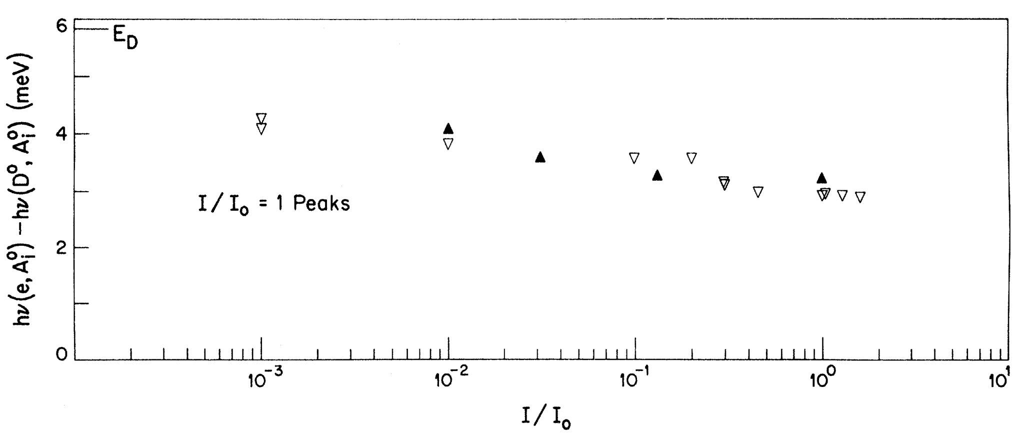

FIG. 3. The solid triangles are the separation in energy (meV) between the 1.4933- and 1.4899-eV transitions as I/I_0 is varied. The open triangles represent the same data for the pair 1.4890 and 1.4861 eV. As I/I_0 is decreased the 1.4899- and 1.4861-eV transitions shift to lower energies causing the increase in separation. The data in Figs. 1 and 2 were taken at $I/I_0=1$.

where κ is the dielectric constant and R_{DA} is the distance between the donor acceptor pair. As discussed by Thomas,[14] at low excitation intensity recombination involving distant pairs is more probable and the Coulomb term $e^2/\kappa R_{DA}$ is less significant. As the intensity increases, the more distant pairs saturate and the recombination peak moves to higher energies.

The temperature behavior of these peaks is also consistent with (D^0, A^0) recombination. The intensity of both peaks decreases as the temperature increases, again consistent with thermal ionization of neutral donors.[13] A small electric field produces the same effect. We also note that Dingle[4,5] using time-resolved spectroscopy has studied recombination in this spectral region and concluded in favor of the donor-acceptor pair model.

The magnetic-field data for these transitions [Fig. 2(b)] show a rather large shift, ~14 cm^{-1} in 40 kG. Using the results of Larsen[15] we have calculated the shift in the ground-state energy of a donor to be only ~7 cm^{-1} in 40 kG. Since we have previously established $\Delta E_A(H) \simeq 0$, the difference between these numbers must be due to a change in term $e^2/\kappa R_{DA}$ in Eq. (4) due to a shift in the recombination from more remote to more closely spaced pairs induced by the magnetic field. This is not unexpected since as the magnetic field is increased the size of the (donor) electron orbit shrinks, favoring recombination of more closely spaced pairs. Although an exact quantitative prediction of this effect is difficult to calculate, the following argument does yield a rough estimate of the magnitude involved. At zero magnitude field, the magnitude of the Coulomb interaction term may be used to estimate $\langle R_{DA} \rangle \sim 400$ Å. The additional shift of ~7 cm^{-1} then corresponds to a change of $\langle R_{DA} \rangle$ to ~310 Å. This is consistent with the calculated donor wave function contraction in a field of 40 kG (Ref. 15).

In conclusion, we have demonstrated the presence of and recombination at two acceptors in high-purity GaAs. These identifications, as well as others,[11] are only made substantive by the utilization of a magnetic field in the photoluminescence studies.

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[1]M. A. Gilleo, P. T. Bailey, and D. E. Hill, Phys. Rev. 174, 898 (1968).

[2]E. H. Bogardus and H. B. Bebb, Phys. Rev. 176, 993 (1968).

[3]J. Shah, R. C. C. Leite, and J. P. Gordon, Phys. Rev. 176, 938 (1968).

[4]R. Dingle and K. F. Rodgers, Jr., Appl. Phys. Lett. 14, 183 (1969).

[5]R. Dingle, Phys. Rev. 184, 788 (1969).

[6]E. W. Williams and H. Bebb, J. Phys. Chem. Solids 30, 1289 (1968).

[7]D. E. Hill, Phys. Rev. B 1, 1863 (1970).

[8]W. Schairer and W. Graman, J. Phys. Chem. Solids 30, 2225 (1969).

[9]C. M. Wolfe, G. E. Stillman, and J. O. Dimmock, J. Appl. Phys. 41, 504 (1970).

[10]Values of $|g_e| \sim 0.53$ and $|g_h| \leq 0.2$ are established combining the results of J. A. Rossi, J. O. Dimmock, C. M. Wolf, and G. E. Stillman, to be published, and W. Duncan and E. E. Schneider, Phys. Lett. 7, 23 (1963).

[11]Rossi, Dimmock, Wolfe, and Stillman, Ref. 10.

[12]G. E. Stillman, C. M. Wolfe, and J. O. Dimmock, Solid State Commun. 7, 921 (1969).

[13]G. E. Stillman, C. M. Wolfe, and J. O. Dimmock, J. Phys. Chem. Solids 31, 1199 (1970).

[14]D. G. Thomas, M. Gershenzon, and F. A. Trumbore, Phys. Rev. 133, 269 (1964).

[15]D. M. Larsen, J. Phys. Chem. Solids 29, 271 (1968).